

Evolution of Laterally Ordered Water Structures on Electrode

Yong S. Chu^{a)}, Tedd E. Lister^{b)}, William G. Cullen^{c)}, Zoltan Nagy^{d)}, Hoydoo You^{e)}

Materials Science Division, Argonne National Laboratory, Argonne, IL 60439

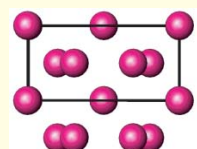
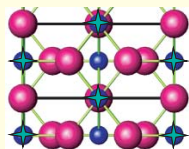
ABSTRACT

The structure and chemistry of interfacial water on metal oxide surfaces are of interest in a wide range of scientific/technical disciplines including oxygen-evolution/reduction chemistry important for future hydrogen economy. However, molecular level experimental studies were hampered in the past by difficulties associated with the bulk water layer that any experimental probe must penetrate. These difficulties can be overcome by advanced x-ray techniques utilizing synchrotron radiation. In this poster, we demonstrate the presence of commensurate, registered water monolayers on the RuO₂(110) surface, using oxygen-sensitive surface x-ray-scattering (oxygen truncation rod) techniques. At anodic potentials close to oxygen evolution, the extraneous water layer and the surface hydroxide layer form a bilayer with O-H-O (symmetric) bonds similar to that of ice X, a high-pressure form of water. At cathodic potentials, the water molecules are converted from the bridging OH molecules to form a low-density O-H...O (asymmetric) bonded water monolayer. These two-dimensional solid water layers at anodic and cathodic potentials provide, for the first time, models indicating precursors for water splitting on an electrode surface to evolve O₂ and H₂, respectively.

Oxygen Truncation Rods (OTR)

Crystal Truncation Rods Sensitive to Surface Oxygen structure

When H+K=odd, Scattering from metal atoms cancel each other leaving crystal truncation rods sensitive only for oxygen atoms.

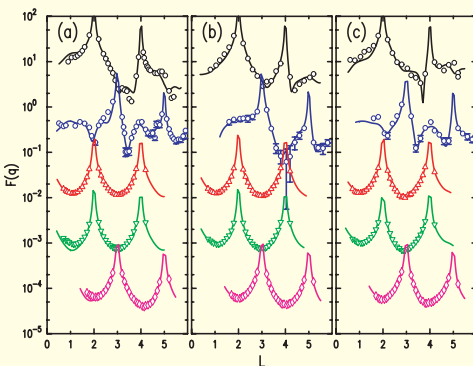


Top view with Ru atoms

The marked atoms are Ru atoms at the top layer. The scattering from Ru atoms in

Without Ru atoms

Scattering from oxygen atoms does not cancel. For OTR, Ru atoms effectively do not exist.

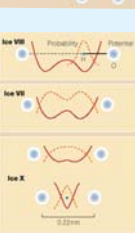


Rod profiles measured at potentials (a) 330 mV, (b) 500 mV, and (c) -200 mV and best fits (solid lines). The black (1,0,L) and blue (0,1,L) rods are the two oxygen truncation rods showing sensitivity to potential.

Ice X and Hydrogen Bonding



Oxygen atom in sp³ hybridization has four possible bonds (solid lines). The covalent bonded hydrogen can also form hydrogen bonds (shown as dashed lines) to neighboring water molecules.



Under ordinary pressure, the hydrogen sits asymmetrically between two oxygen atoms with a covalent bond and a hydrogen bond. At an extreme pressure, the potential well for the hydrogen atom changes from a double-well shape to a single-well shape, known as ice X. At 0.5 eV, an electric field of GV/m is applied at the interface enough to exert such high pressure.

Life Cycle of a Water Molecule on an Electrode: Technological progress towards a future hydrogen economy relies on understanding molecular-level phenomena governing conversion of water to hydrogen and back at the electrodes in electrolyzers and fuel cells. Ruthenium and ruthenium oxide are particularly interesting in this regard since they are unsurpassed at enhancing catalytic activities in low-temperature fuel cell anodes. Ruthenium combined with platinum is a very promising electrocatalyst for hydrogen oxidation and oxygen reduction reactions, potentially allowing pollution-free and cost-efficient production and oxidation of hydrogen. We chose to study single-crystal surfaces of RuO₂ as a model electrode to elucidate, in unprecedented molecular-level details, the water splitting and recombination reactions on an electrode. In a series of synchrotron x-ray studies, we discovered fascinating sequential rearrangements of surface water molecules, evolving from a loose hydrogen-bonded water layer, to a hydroxide layer, and to a dense form of water, which exist on the RuO₂(110) surface at different applied potentials. These interfacial forms of water may be the intermediates long suspected to be responsible for promoting oxidation of hydrogen and methanol in the fuel-cell environment as well as promoting the oxygen-reduction reaction. These, previously unavailable, molecular-level details of the water-conversion processes are expected to provide scientific impetus for a more rational design of high performance electrocatalysts. This first-of-its-kind study was possible because of the unprecedented level of sensitivity afforded by the high brilliance of x-rays at the Advanced Photon Source.

Models for Solid Water Layer [1]:

There are two charge-transfer reactions in a voltammogram shown in Fig. 1. Therefore there are three surface oxidation states, denoted as I, II, and III and the corresponding model structures based on OTR measurements are shown in Fig. 2. Only the oxygen positions were determined, and the species identification (i.e., O, OH, or H₂O) was conjectured. In the structure II at 330 mV, all Ru atoms are terminated with OH⁻ with the charge neutrality. In structure I, every other row of OH is converted to water which is trapped and anchored via hydrogen bonding between the remaining rows of OH's. A large hysteresis loop of the x-ray intensity (blue dots), approximately proportional to the height of the water molecules remaining at their 'birth' sites, is observable between 330 and -1200 mV. Around -300 mV, the height of the water molecules reaches a maximum near zero field. At negative potential to this, the attraction of hydrogen atoms to the surface leads to adsorption on the surface and a slightly lower potential allows the water molecules to split, resulting in H₂ evolution. A reversal of the polarity does not automatically restore the lost hydrogen network and registry until the potential reaches that of A1 peak where OH is chemisorbed back to Ru atoms.

The oxidation of structure II at A_{II} peak leads to the 500-mV bilayer structure. The lateral water-water distances are

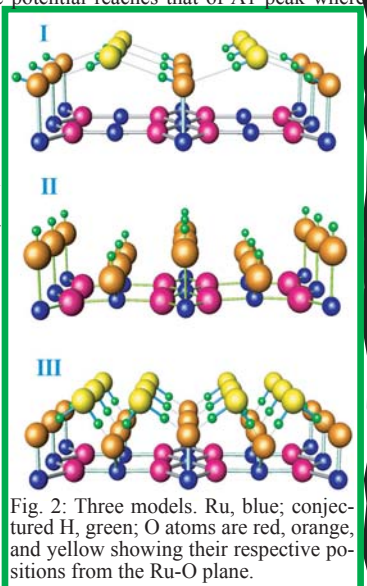


Fig. 1: Upper: Cyclic voltammogram I, II, and III mark the potentials for the respective structure models shown in Fig. 2. Lower: X-ray intensity of OTR shows a remarkable hysteresis.

essentially locked to the underlying lattice but the interlayer separation is in the range of 2.2 to 2.4 Å and the hydrogen is expected to be centered in an effective single-well potential like in ice X. At slightly higher potentials, the centered hydrogen atoms likely escape, allowing the oxygen atoms to bond directly, resulting in O₂ evolution. All the main features of our experimental results have been confirmed in recent theoretical studies [2].

Current addresses:

- Experimental Systems Division, Advanced Photon Source, ANL
- Idaho National Engineering and Environment Laboratory
- Materials Research Science and Engineering Center, U of MD.
- Guest Senior Scientist, retired in 2001.
- Corresponding author: hyou@anl.gov.

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